Influence of Light and Temperature on the Extractability of Cerium(IV) as a Surrogate of Plutonium(IV) and its Effect on the Simulation of an Accidental Fire in the PUREX Process

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ⓈSupporting Information

ABSTRACT: Modeling of plutonium(IV) behavior during an accidental fire in a reprocessing plant was considered using various non-radioactive metallic surrogates. Among those elements, cerium(IV) was supposed to be a suitable candidate due to possible formation of a complex with TPB, but its extractability and stability have not been studied previously under representative plutonium uranium reduction extraction (PUREX) conditions. In this work, we investigated the chemical analogy between cerium(IV) and plutonium(IV) in this extractive process and combustion thereof. Distribution

ratios are reported for acidities of 1−4 mol L^{-1} in equal volumes of nitric acid and a 30:70 mixture of tributylphosphate and hydrogenated tetrapropylene. The influences of light, temperature, and extraction time were studied by UV−vis spectroscopy. The results showed that cerium(IV) is extracted quantitatively but is reduced over time to cerium(III) in the organic mixture. Spectrophotometric investigations of this reaction kinetics revealed an apparent rate constant k of 0.021 ± 0.002 mol$^{0.5}$ L$^{0.5}$ min^{-1} at 298 K and an apparent fractional reaction order of 0.5. The activation energy of this reduction was found to be around 82 ± 2 kJ mol^{-1} by the Arrhenius plot method. The combustion of mono- and biphasic solutions prepared with a cerium(IV) concentration of 10 g L^{-1} revealed that the extracted complexes, Ce$_2$O·6NO$_3$·3TBP$_{(org)}$ or Ce$_4$O$_4$·8NO$_3$·6TBP$_{(org)}$, are reduced during the combustion. Compositions of the resulting ashes and soot were analyzed and highlighted the presence of pyrophosphates and polycyclic aromatic hydrocarbons, with some traces of cerium. Ce(IV) is not suitable to represent Pu(IV) from a chemical point of view in HNO$_3$/TBP−HTP solutions.
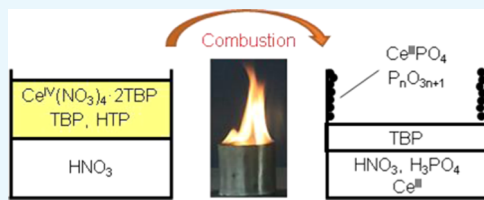
■ INTRODUCTION

Nuclear waste treatment is of primordial importance to reduce the volume of fissile materials stored in the environment and to allow their recycling. For many years, several methods have been developed to fulfill this task, such as evaporation, precipitation, extraction, ion exchange and membrane processes.[1] Among them, the plutonium uranium reduction extraction (PUREX) process is a Pu^{4+} and UO$_2^{2+}$ reprocessing technique based on their extraction from nitric acid medium. Tributylphosphate (TBP) is generally used as an extractive agent in combination with diluents, such as dodecane, kerosene, or hydrogenated tetrapropylene (HTP), which is a branched C12 alkane (2,4,6-trimethylnonane, C$_{12}$H$_{26}$).[2] This process is largely developed on a plant scale in several countries to recycle spent nuclear fuels. The HTP diluent was chosen because of its industrial use in the French reprocessing factory at La Hague (ORANO company). However, fire or explosion hazard is a serious concern in nuclear reprocessing factories due to the flammable nature of the solvent mixture.[3] Since released radioactive materials could potentially leak through aerosol clouds during a fire, appropriate modeling of this phenomenon should be considered.

A representative simulation of an accidental fire occurring during the PUREX process would allow the prediction of fire behavior and airborne radioactive releases. The model would ideally allow limiting or preventing the impact of any accidental environmental discharge of radioactive material. Several elements such as Ce(IV), Zr(IV), and Hf(IV) have been proposed and studied to simulate Pu(IV) in nuclear waste extraction studies.[4−6] Among these candidates, cerium-

(IV) has been considered a suitable surrogate of plutonium-(IV) for fire modeling because Ce(IV) possesses an ionic radius of 0.97 Å, which is very close to the radius of Pu(IV) (0.96 Å)[5] and, as detailed below, may form some complexes with TBP and be stable in the organic phase. For plutonium-(IV), it can be extracted in nitric acid medium by TBP in high yield (ca. 95%), forming some coordination complexes of the general formula, $M^{IV}(NO_3)_4 \cdot nTBP$ (bi-capped anti-prismatic geometry) with $n = 2$ for Pu.[5,7,8]

Extraction of cerium(IV) from nitric acid medium has been extensively studied in the literature with various solvents, such as ethyl ether,[9] nitromethane,[10] di(2-ethylhexyl) 2-ethylhexyl phosphonate (DEHEHP),[11] Cyanex-923,[12] TBP,[7,13] or even ionic liquids, such as $[C_8mim]PF_6$ (1-octyl-3-methylimidazolium hexafluorophosphate).[14] However, the study of cerium-(IV) extraction in a mixture of TBP and HTP, which is an alkane diluent of industrial interest used in the PUREX process,[15−18] has never been documented. TBP is a well-known extractant, which acts in a first reaction model as a monodentate ligand for the cerium(IV) cation and allows its migration from an aqueous to an organic phase as follows[19]

$$(Ce)^{4+} + 4NO_3^- + 2\,TBP_{(org)} \rightarrow Ce(NO_3)_4 \cdot 2TBP_{(org)}$$

However, very recent studies by Antonio et al. indicated a revisited reaction scheme involving the occurrence of the formation of cerium(IV)−tributylphosphate complexes with unexpected nuclearities. The formation of dinuclear $Ce_2O \cdot 6NO_3 \cdot 3TBP_{(org)}$ or tetranuclear $Ce_4O_4 \cdot 8NO_3 \cdot 6TBP_{(org)}$ has been observed by a combination of XANES, EXAFS, and SAXS measurements.[20,21] This clearly shows that the monomeric system does not exist in solution with nitric acid and TBP. In the rest of the paper, the Ce(IV) complexes in the organic phase will be denoted as $Ce(IV)−NO_3−TPB_{(org)}$.

Previous studies highlighted the effect of concentration of various components, such as cerium, nitrate, acid, and TBP, and the choice of diluent on extraction yields.[7,8,10,13,22] A study by Sakamoto et al. mentioned that cerium(IV) is back-extracted when exposed to light but the reaction was not documented further.[23] Another report by Friedrich et al. briefly examines the reduction rate of the extracted cerium(IV)−TBP complex in various diluents, such as benzene and cyclohexane.[24] This report mentions reduction speeds between 7 and 15 mg mL^{-1} h^{-1}, but there is no mention of a reaction mechanism and thermodynamic or kinetic study.

Beyond the identification of Pu(IV) surrogates in terms of the PUREX extraction process, one of the major remaining questions while investigating consequences of fire in terms of radioactive material dispersion is the representativeness of such surrogates even under thermal stress and degradation of HTP/TBP-contaminated organic solutions. As far as we are concerned, there is no consensus on the ideal surrogate for mimicking the behavior of Pu(IV) extracted in the HTP/TBP phase during a fire scenario. As previously mentioned, cerium(IV) has been largely considered in previous studies for investigating airborne release of plutonium during accidental fires. From an experimental point of view, among six studies summarized by Quintiere[25] for fires involving liquid fuels, three have been carried out by considering cerium(IV) as a surrogate.[26−28] However, cerium(IV) is known for its high oxidizing power and could potentially be reduced to cerium(III) during or after extraction and fire, which would not be truly representative of plutonium(IV) behavior. Then,

the question of its relevance as a plutonium(IV) surrogate, in terms of airborne release in the event of a fire, representative of the PUREX process, is still under consideration.

Thus, the purpose of this work follows different directions of investigation. Our first aim was the study of cerium(IV) stability in both aqueous and organic phases. Second, we sought to simulate plutonium(IV) extraction by cerium(IV) and to evaluate distribution coefficients under various conditions, specific to the PUREX process. Finally, to get a better understanding of solvent fires without the hazards resulting from the use of radioactive materials, we studied cerium(IV)-containing solvent combustions involving a mixture of HTP, TBP, and aqueous nitric acid solution and evaluated the amount of cerium(IV) that was potentially released as aerosol clouds. Thus, the first part of this study deals with the investigations of cerium(IV) stability and extractability in a biphasic organic−water system consisting of an aqueous nitric acid solution for the first phase and a mixture of HTP and TBP at a 70:30 ratio (volume) for the second one. The influence of temperature, acidity, light, and contact time on the extraction yields and distribution ratios is reported. The stability of the $Ce(IV)−NO_3−TPB_{(org)}$ complexes was also investigated by spectrophotometry, and a kinetic study was undertaken. The second part is focused on the combustion of mono- and biphasic systems containing cerium(IV). It was examined in detail along with aerosol analysis and cerium distribution in both aqueous and organic solutions.

■ RESULTS

Extraction of Cerium(IV) from an Aqueous Nitric Acid Solution to a TBP/HTP Mixture. To determine the distribution ratios of cerium(IV) and to compare them with plutonium(IV) values, we adopted representative conditions of a PUREX extraction procedure.[2] Therefore, distribution ratios were evaluated for 10 g L^{-1} cerium(IV) concentration in the presence of equal volumes of nitric acid (aqueous phase) and a 30% TBP and 70% HTP solvent mixture (organic phase). Partitions were carried out in a thermostat for 10 min with magnetic agitation to ensure a constant temperature of the extraction medium and good contact between the two phases. Cerium concentration for each of the two organic and aqueous phases was then determined by means of a spectrophotometric method based on Arsenazo-III.[29] The influence of temperature, acidity, presence or absence of light, and extraction time has been studied. Our results are summarized in Figures 1 and 2.

Cerium(IV) is quantitatively extracted in 10 min from nitric acid medium by the TBP/HTP mixture, with partition yields varying between 82 and 98% for a single extraction (Figure 1a). Distribution ratios, defined as the concentration of organic cerium divided by aqueous cerium (see the Supporting Information for details), were calculated and vary between 4 and 59 (Figure 1b), which is in the same range as in other cerium(IV) partition studies with pure TBP[30] (D_{Ce} = 8 to 14) or TBP diluted with dodecane[13] or hexane[8] (D_{Ce} = 7 and 26, respectively). In comparison to cerium(IV) under similar conditions, plutonium(IV) displays distribution ratios between 2 and 24 at 1 and 4 M nitric acid concentration, respectively.[31] These results indicate that HTP, which acts as a solvent agent, does not significantly disturb the extraction efficiency. Thus, cerium(IV) is highly extractable and can be representative of plutonium(IV) behavior under PUREX process conditions.
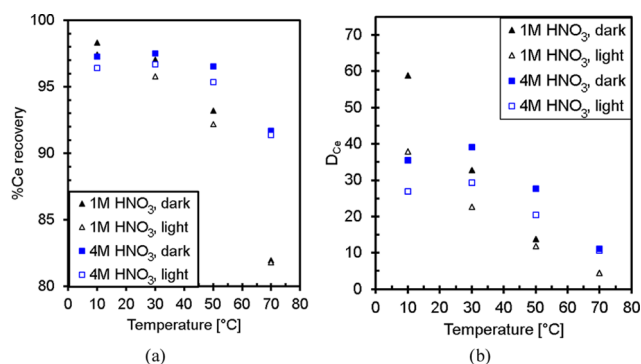
Figure 1. (a) Partition yields and (b) distribution ratios of cerium(IV) as a function of temperature at a nitric acid concentration of 4 M (blue squares) or 1 M (black triangles) and in the dark (filled symbols) or in the presence of light (open symbols) for 10 min contact between the two phases.
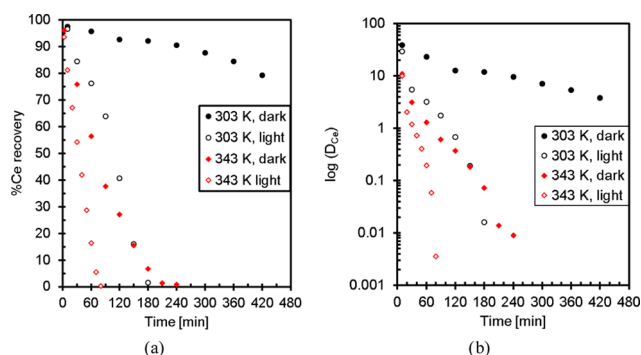

Figure 2. (a) Partition yields and (b) distribution ratios of cerium(IV) as a function of time at 303 K (black circles) or 343 K (red diamonds) and in the dark (filled symbols) or in the presence of light (open symbols) at a nitric acid concentration of 4 M.

The influence of nitric acid concentration seems to be correlated with the temperature. At 10 °C, a lower nitric acid concentration favors Ce(IV) extraction, whereas at higher temperatures (30−70 °C), a higher nitric acid concentration is slightly more beneficial. This can be rationalized by the fact that higher acidities are linked with a higher concentration of the organic complex, TBP·HNO$_3$, and, therefore, a lower availability of free TBP for cerium(IV) extraction. Light exposure is also a prevailing factor between 10 and 50 °C and significantly decreases cerium(IV) extraction yields. If the temperature increases up to 70 °C, the extraction yields are not appreciably diminished by light exposure and substantially drop for all experiments, regardless of the acidity. These observations indicate that cerium(IV) extraction is negatively affected by heat and light. Both effects are ascribed to the reduction of cerium(IV) under the influence of heat or light and its back-extraction to the aqueous phase. Our results are in agreement with previous reports, highlighting the catalytic role of light in the cerium(IV) reduction process,[23,24] although this effect was not always clearly stated in most extraction studies.[7,8,10,13,22]

As a consequence, we studied the influence of contact time on distribution ratios at a nitric acid concentration of 4 mol L^{-1}. As presented in Figure 2a, partition yields significantly drop after a few hours, particularly in the presence of light or heat. After 1 h, the extraction yield at 303 K is 76% for a solution exposed to light, whereas it stays as high as 96% in the

dark. For the same lapse of time, a solution heated at 343 K presents an extraction yield of 57% in the dark or 16% with light. In fact, reduction of the Ce(IV)−NO$_3$−TPB$_{(org)}$ complexes followed by back-extraction occurs quickly and can be followed visually by the disappearance of the yellow color, characteristic of cerium(IV) (Figure S1). When the effects of light and heat are combined, the extracted cerium(IV) is quantitatively reduced to cerium(III) in less than 2 h at 343 K and migrates back to the aqueous phase. This reduction is also observed in the dark, although at a much lower rate, i.e., after 4 h at 343 K and more than 24 h at 303 K. Therefore, an in situ spectrophotometric study was undertaken to further evaluate the reaction kinetics and order.

Spectrophotometric Investigations of the Kinetics of Degradation of Cerium(IV) in the TBP/HTP Mixture. The stability of cerium(IV) in the biphasic extraction medium was investigated. Since cerium(IV) has a relatively high standard potential ($E^0 = 1.61$ V in 1 M nitric acid),[32] it can be subject to reduction by compounds such as nitrous acid, water, or ammonia. Therefore, cerium(IV) stability in a monophasic nitric acid phase was evaluated to ensure that it is not subject to reduction before extraction. Our results indicate that cerium(IV) is very stable in 4 M nitric acid for several days at 343 K and that no reduction process takes place under our conditions (Figure S2), in agreement with the reported literature.[33] Since the distribution ratios decrease as a function of time, it actually appears that the extracted species, either Ce$_2$O·6NO$_3$·3TBP$_{(org)}$ or Ce$_4$O$_4$·8NO$_3$·6TBP$_{(org)}$, are unstable. Therefore, the compound was synthesized by combining CAN with an excess of 2 equiv of TBP, and its reduction rate was studied spectrophotometrically in the dark at five different temperatures (287, 293, 298, 303, and 307 K).

The absorbance of the cerium(IV) complex was recorded at 325 nm at various time intervals in a mixture of TBP and HTP saturated with nitric acid and water beforehand (see Figure S3 for the full spectrum of the solvent mixture). The cerium(IV) complex decomposes steadily at 303 K in the dark (Figure 3a).
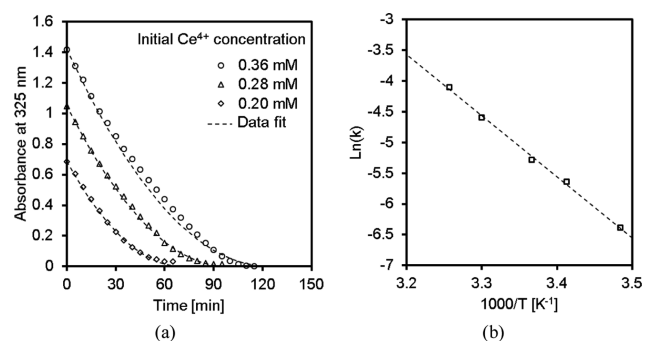

Figure 3. (a) Absorbance change of the Ce(IV)−NO$_3$−TPB$_{(org)}$ complex at 325 nm as a function of time at various cerium(IV) concentrations. Dashed lines represent the experimental fitting of the curves. (b) Arrhenius plot for the reduction of the Ce(IV)−NO$_3$−TPB$_{(org)}$ complex in the organic phase.

Experimental data could not be modeled via zero-, first-, or second-order kinetics and was therefore fitted to a fractional order (see the Supporting information for further details). The apparent rate constant k for this reaction is 0.021 ± 0.002 mol$^{0.5}$ L$^{0.5}$ min^{-1} (303 K), with a fractional reaction order of 1/2, confirming the existence of multinuclear Ce(IV) complexes.[21] Such a fractional reaction order is characteristic of

Table 1. Evolution of Cerium Distribution and Volumes of Nitric Acid, TBP, and HTP during a Biphasic Solvent Fire

combustion time (s)	TBP[a] (mL)	HTP[a] (mL)	HNO$_3$ (mL)	% mass Ce$_{org}$	% mass Ce$_{aq}$	H$_3$PO$_4$ presence[b]
0	12.0 ± 1.0	28.0 ± 1.0	40.0 ± 1.0	99.4 ± 4.1%	0.6 ± 4.2%	negative
120	11.3 ± 1.0	23.2 ± 1.0	38.0 ± 1.0	74.2 ± 3.9%	15.3 ± 3.3%	negative
240	11.2 ± 1.0	13.8 ± 1.0	38.0 ± 1.0	44.8 ± 4.6%	43.0 ± 3.3%	negative
360	10.5 ± 1.0	4.5 ± 1.0	34.0 ± 1.0	2.8 ± 3.9%	89.2 ± 3.3%	positive
480	10.5 ± 1.0	2.0 ± 1.0	33.5 ± 1.0	2.6 ± 4.0%	86.8 ± 3.5%	positive

[a]Composition of the organic phase was evaluated by ^{1}H NMR and integration of the corresponding solvent peaks. [b]The presence of phosphate in the aqueous phase was highlighted with a qualitative molybdate test.
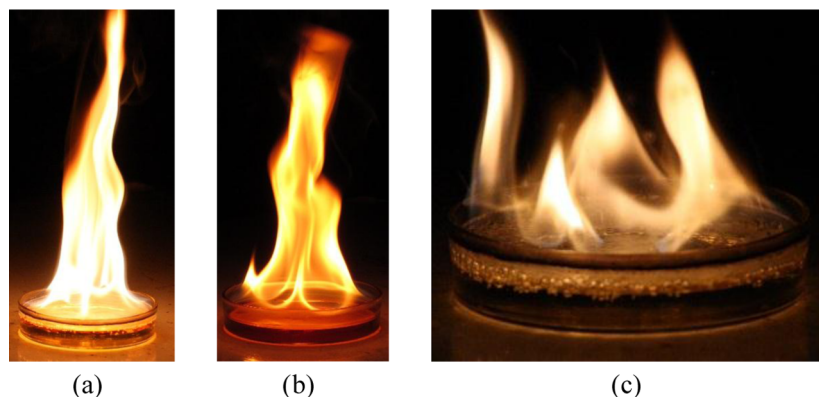

Figure 4. Still images of the combustion of (a) a biphasic HTP/TBP and nitric acid mixture and (b) a monophasic HTP/TBP mixture, (c) ebullition of the aqueous medium in a biphasic fire.

complex mechanisms and shows that the cerium(IV) complex might be involved in several simultaneous reactions.

In fact, different reactions could potentially explain this reduction behavior. The dissociation of CAN by photolysis into cerium(III) and a nitrate radical was previously studied by the group of Baciocchi.[34,35] However, this mechanism seems unlikely in our case, since nitrate radical formation occurs only by flash photolysis. Previous studies with highly oxidizing americium(VI) (E^0 AmO$_2$$^{2+}$/AmO$_2$$^+$ = 1.62 V)[36] or chromium(VI) (E^0 HCrO$_4$$^-$/Cr^{3+} = 1.35 V)[32] have shown that the organic TBP/diluent mixture seems to play a reducing role toward both elements in such an extraction medium.[37−39] In fact, the standard potential of the redox couple Ce(IV)−TBP/Ce(III)−TBP was evaluated to be between E^0 = 1.356 V and E^0 = 1.416 V vs Ag/AgCl depending on the concentration of cerium(IV),[20] further emphasizing the oxidative power of cerium(IV). Thus, it appears that the Ce(IV)−TBP complexes react with solvent molecules, yielding cerium(III) that is quickly back-extracted to the aqueous phase.

To get further insight into the reaction, we recorded the absorbance of the Ce(IV)−NO$_3$−TPB$_{(org)}$ complexes at 325 nm as a function of time at various temperatures (Figure S4). Experimental values were fitted to determine the corresponding apparent rate constants and evaluate the activation energy by Arrhenius plots over the temperature range of 287−307 K (Figure 3b). The activation energy was found to be around 82 ± 2 kJ mol$^{−1}$, which is significantly high and confirms that this back-extraction process is controlled by a chemical reaction. In fact, the activation energy corresponding to the stripping of iron(III) from a di-2-ethylhexyl phosphoric acid (D2EHPA) and TBP mixture with oxalic acid was found to be around 77 kJ mol$^{−1}$.[40] On the other hand, the stripping of plutonium(IV) by dihydroxyurea (DHU) in a system of 30% TBP/kerosene and HNO$_3$ is controlled by diffusion and shows a much lower activation energy of 28 kJ mol$^{−1}$.[41]

Study of the Combustion of Biphasic and Monophasic Systems Containing Cerium(IV)−TBP and Nitric Acid. To evaluate the validity of cerium(IV) as a surrogate of plutonium(IV) during solvent fires, we designed experimental combustion experiments under PUREX conditions. Care was taken to avoid heat or light exposure of the solutions and to avoid cerium(IV) reduction before ignition. First, a kinetic study of a biphasic solution fire was performed by extinguishing the fire at various time intervals to evaluate cerium reduction and airborne release as a function of time. Results are presented in Table 1. Since the PUREX process requires the separation of organic and aqueous materials, the combustion of a single organic phase after extraction of cerium(IV) was studied as well. Cerium(IV) concentration was set at 10 g L$^{−1}$ in 4 mol L$^{−1}$ nitric acid to represent a typically high Pu(IV) concentration in an industrial configuration. Equal volumes of an aqueous nitric acid phase and an organic TBP/HTP phase were mixed and equilibrated. The mixture was stored away from light or heat to avoid cerium(IV) reduction until ignited with a propane blowtorch under an ambient atmosphere. Residual samples of the organic phase, aqueous phase, aerosol, and ashes were collected during combustion and at the end of the fire for ICP-MS analysis, mass spectrometry, infrared spectroscopy, ^{1}H and ^{31}P NMR, spectrophotometric cerium content analysis, powder X-ray diffraction analysis (PXRD), and scanning electron microscopy (SEM).

Observation of the combustion in either monophasic or biphasic fires shows a large flame oscillating around the container and with a regular behavior through time (Figure 4). Unlike combustion of towels impregnated with ceric ammonium nitrate, which present a blue color,[42] our flames displayed a yellow/orange color typical of hydrocarbon fires. The mean combustion duration for a biphasic mixture of 40 mL of HTP/TBP and 40 mL of nitric acid was approximately

495 s for a circular 255 cm^2 surface. In the case of a monophasic fire, combustion ended when the TBP/HTP mixture was completely consumed, and the total fire duration was slightly longer, i.e., 538 s. Boiling of the aqueous phase was observed in the biphasic fire halfway through the combustion (approximately 240 s), with projection of liquid droplets around the container (Figure S5). The temperature of the aqueous medium was followed with the help of a thermocouple and showed a linear increase with time from 15 to 100 °C in 8 min (Figure S6). Therefore, projection of liquid droplets can be explained by heat transfers through the solution that also result in a boilover of nitric acid that extinguishes the combustion. Therefore, the combustion ends spontaneously when the organic layer is thin enough for the flame to contact the aqueous phase.

The composition of the remaining organic phases after biphasic combustions was examined in detail with ^{1}H and ^{31}P NMR along with cerium quantification by spectrophotometric analysis. Details of the NMR spectra from the remaining liquid samples are available in the Supporting Information (Figure S7). No combustion byproduct is revealed, although the initial TBP/HTP ratio largely shifts during the fire (Table 1). In fact, the final TBP/HTP volumetric ratio is approximately around 3:0.6 versus 3:7 initially, highlighting a rapid and almost quantitative HTP combustion. Although the initial cerium(IV) concentration in the organic phase is around 9.90 g L^{-1} after extraction, it decreases drastically during combustion. Organic cerium concentration after combustion is typically between 0.85 and 0.94 g L^{-1}, which indicates that the Ce(IV)−NO$_3$−TPB$_{(org)}$ complexes are largely reduced during the experiment by the effect of both light and heat and migrate back to the aqueous phase (see below).

The aqueous phases were analyzed as well and showed a slight variation of volume during fire, due to the evaporation of water from the combustion medium (Table 1). ^{1}H NMR analysis of aqueous phases showed again no sign of degradation products. However, an ammonium molybdate test highlights the presence of phosphoric acid with formation of a yellow precipitate of phosphomolybdate.[43] Therefore, phosphoric acid is a degradation product of TBP that migrates to the aqueous phase during the combustion. Cerium content in the aqueous phases was determined and showed a significant growth during combustion. In fact, aqueous cerium concentration, which is initially around 0.10 g L^{-1} after extraction, increases up to 11.1 g L^{-1} after combustion and evaporation. This can be explained by the reduction and back-extraction of organic cerium during solvent fire. As can be seen in Table 1, this reduction process occurs in an almost linear way. Boiling of the combustion mixture could facilitate the rapid back-extraction of cerium(IV) by increasing contacts between the two phases, in addition to the temperature effect.

The residual ashes from the combustion of a monophasic TBP/HTP system were analyzed by scanning electron microscopy (SEM) and revealed an irregular granular surface (Figure 5). The magnified images showed small grains of micrometer size, forming a flat surface with a few cracks. The crystallinity of the residual ashes inside the combustion container was evaluated with the help of PXRD analysis. Most samples showed very low crystallinity or no crystallinity at all (Figure 6). Comparison of our PXRD diagrams with the theoretical monazite powder diffractogram demonstrates that the combustion residues could contain slightly crystalline monazite Ce^{III}PO$_4$. The presence of this compound can be
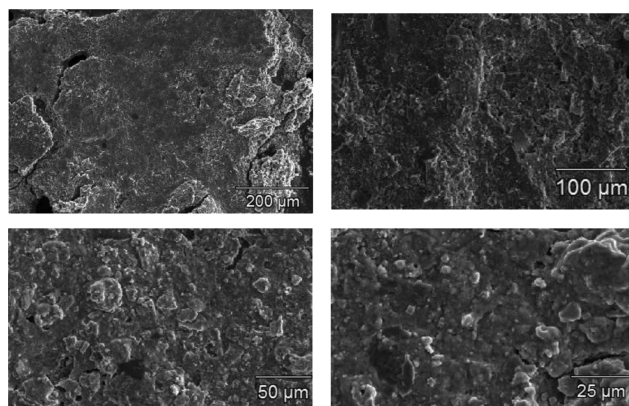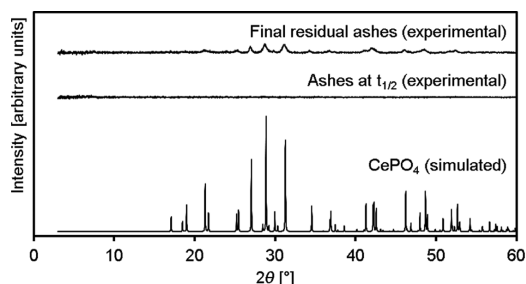

Figure 5. SEM analysis of ash particles.

Figure 6. PXRD diagrams of monazite and ashes of a biphasic fire at two different time intervals.

rationalized by the combination of reduced cerium(IV) and degradation of TBP into phosphoric acid.[44] The presence of monazite was further confirmed by infrared analysis, with characteristic molecular vibrations of coordinated phosphate tetrahedra around 1000 cm^{-1} (Figure S8).[45]

Mass spectrometry was performed on ashes to further investigate their compositions (see Figures S9 and S10). In positive mode, the spectrum showed peaks of TBP and its decomposition products with m/z = 267 (tributylphosphate, HTBP$^+$), 211 (dibutylphosphate, H$_2$DBP$^+$), and 155 (mono-butylphosphate, H$_3$BP$^+$).[44] Further degradation of TBP into phosphates is confirmed by the presence of peaks relevant to H$_4$PO$_4^+$ (m/z = 98), H$_2$PO$_3^+$ (m/z = 80), and H$_2$PO$_2^+$ (m/z = 65). Smaller alkyl fragments can be identified at m/z = 27 (C$_2$H$_3^+$), 29 (C$_2$H$_5^+$), 39 (C$_3$H$_3^+$), 41 (C$_3$H$_5^+$), 55 (C$_4$H$_7^+$), and 57 (C$_4$H$_9^+$). Polycyclic aromatic hydrocarbons (PAHs), which are produced during combustion, are detected as well at m/z = 127 (C$_{10}$H$_7^+$), 178 (C$_{14}$H$_{10}^+$), and 252 (C$_{20}$H$_{12}^+$). Negative mode reveals the presence of numerous pyrophosphate anions of the general formula, P$_n$O$_{3n+1}$, at m/z = 158, 176, 194, 238, 256, 274, and 292. These compounds are formed after degradation of TBP into phosphoric acid and polymerization thereof.

In addition to analyses of organic/aqueous solutions and ashes, released particles in the airborne phase were sampled by filtration and using high-efficiency particulate air membranes and TEM grids. Surfaces of samples were imaged and SEM micrographs as well as EDX spectra were recorded, revealing a significant cerium content for each considered particle. More than 30 particles were detected on sampling substrates associated with the biphasic condition. For all detected particles, EDX analysis has confirmed that released particles are mainly composed of cerium, phosphorus, and oxygen (see
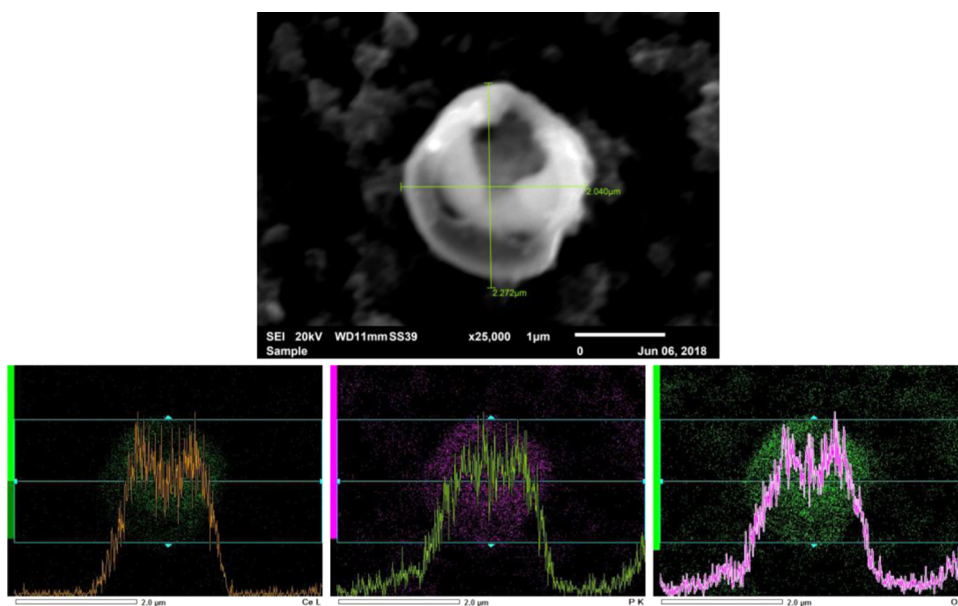
Figure 7. SEM image and corresponding Ce, P, and O distributions measured by EDS.

Figure 7). This phosphate composition ($Ce_xP_yO_z$) is in close agreement with the small content of monazite in the residues reported by PXRD analysis. One must also notice that particles containing cerium are fully isolated from carbonaceous particles produced during TBP/HTP combustion.

In addition to elemental composition, each particle was analyzed in terms of equivalent diameter and circularity. Particle equivalent diameter was determined using the SEM image by measuring the maximum length (L) and width (W) of the particle (see Figure 7). The corresponding diameter is then defined as the arithmetic mean between length and width. Circularity of each particle was also investigated by determining the ratio between L and W, with circularity close to 1 corresponding to a quasispherical non-elongated particle.

Figure 8 presents the size distribution for the biphasic condition and its log-normal fitting. The median equivalent
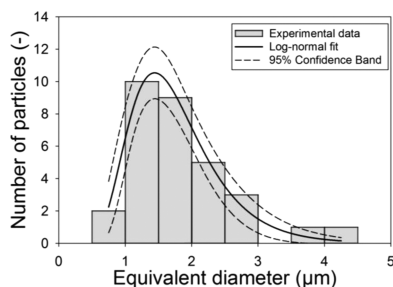

Figure 8. Particle size distribution in terms of equivalent diameter for cerium particles released under the biphasic condition.

diameter of the released cerium particles is close to 1.66 ± 0.09 μm (95% confidence interval) with a relatively narrow size distribution (geometric standard deviation of 1.45 ± 0.07). Mean circularity is also computed and is close to 1.35 ± 0.78 (95% confidence interval), denoting an elongated shape for most particles.

According to the size distribution and composition of released particles, the assumption of resuspension mainly

driven by pool boiling phenomena and drying of ejected micron-sized droplets was considered.[42,43] For this purpose, the following hypotheses were assumed:

- bubble diameter in the range 0.1−1 mm (as noticed on videos recorded during combustion experiments),
- release of particles mainly driven by drying of film droplets, which are assumed to be the most probable for an initial bubble diameter ranging from 0.1 to 1 mm,[43,44]
- jet droplet diameter D_{jet} ranging from 10 to 100 μm,[45]
- cerium concentration in the organic phase rapidly decreasing from 10 to 1 g L^{-1}, corresponding to a final organic $CePO_4$ concentration C_{CePO_4} of 1.7 g L^{-1}.

According to all of these assumptions, diameter D_p of a $CePO_4$ particle produced by drying of such contaminated jet droplets was estimated with the following relationship and assuming the $CePO_4$ density ρ_{CePO_4} to be equal to 5220 kg m^{-3}

$$D_p = D_{jet} \sqrt[3]{\frac{C_{CePO_4}}{\rho_{CePO_4}}}$$

The geometric diameter computed according to these assumptions ranges from 0.7 to 6.8 μm. These values are in reasonable agreement with the median diameter reported from SEM analysis (see Figure 8), confirming that the release is mainly driven by bursting of bubbles.

■ CONCLUSIONS

In this paper, we highlighted the influence of acidity, light, and heat on cerium(IV) extraction yields and distribution ratios. After initial complexation with TBP and partition from the nitric acid medium, the set of $Ce_2O\cdot6NO_3\cdot3TBP_{(org)}$ or $Ce_4O_4\cdot 8NO_3\cdot6TBP$ complexes is quickly reduced, which is reflected in diminishing distribution ratios. A spectrophotometric study of the reduction phenomenon showed that it occurs spontaneously and is accelerated by the presence of light or heat. A kinetic study showed that the $Ce(IV)-NO_3-TPB_{(org)}$ complexes are subject to rapid reduction and back-extraction and follow a fractional 1/2-order kinetic model with an

apparent rate constant of 0.021 ± 0.002 mol$^{0.5}$ L$^{0.5}$ min^{-1} at 298 K. The combustion of a mixture made of HTP/TBP, nitric acid, and CAN revealed that organic cerium(IV) was reduced from the organic phase during the fire. The cerium content in the aqueous phase increased drastically during the combustion by transfer from the organic phase. TBP degradation was also observed, which resulted in the evolution of phosphoric acid that recombined with cerium(III) to form poorly crystalline monazite ashes collected on the container. Particles released in the airborne phase were also analyzed by SEM/EDS, highlighting median particle diameters of nearly 2 μm and a composition with major contributions of Ce, P, and O elements. This study allowed us to evaluate the capability of cerium(IV) as a simulating agent for plutonium(IV) in the PUREX extraction process and accidental fire thereof. Although cerium(IV) is highly extractable in a biphasic nitric acid and TBP/HTP mixture, cerium(IV) cannot be considered as a relevant chemical surrogate of Pu(IV) due to its rapid reduction into Ce(III) during the combustion process in contrast to Pu(IV) with Pu(NO$_3$)$_4$·2TBP which is very stable toward light and heat. The two main open questions are as follows: (i) Do the quantities of plutonium released during combustion depend significantly on the distribution ratio between the aqueous and organic phases? (ii) Can plutonium, like cerium, be released as plutonium phosphates? These points should be further addressed.

■ EXPERIMENTAL SECTION

Experiments were conducted using the following chemical reagents: cerium ammonium nitrate ((NH$_4$)$_2$Ce(NO$_3$)$_6$, denoted as CAN, Aldrich, ≥98.5%), tributylphosphate (denoted as TPB, Aldrich, ≥99%), hydrogenated tetrapolypropylene (mixture of branched alkanes of the general formula, C$_{12}$H$_{26}$, denoted as HTP, from the ORANO La Hague plant, France, CAS Number 68551-17-7), nitric acid (HNO$_3$, Aldrich, 65%), and deionized water. Other reactants were purchased from Aldrich for the quantitative chemical analysis of Ce^{4+}/Ce^{3+} solutions: silver oxide (Ag$_x$O), Arsenazo-III, sodium oxalate (≥99.5%), glycine (≥99%), L-ascorbic acid, and hydrochloric acid (HCl, 37%). All chemical reagents (except HTP) are commercially available and were used without any further purification.

UV−Vis Spectroscopy. UV−vis spectra of the samples were collected using a PerkinElmer Lambda 650 spectrophotometer. The kinetic study was undertaken at a constant temperature with a thermostated cell holder linked to a thermoregulation apparatus. The temperature inside the cell was checked before and after the experiment. A known quantity of the synthesized Ce(IV)−NO$_3$−TPB$_{(org)}$ complexes was injected inside a mixture of TBP/HTP (volume ratio 30:70) pre-equilibrated with nitric acid. The absorbance of the yellow complex was followed at a constant temperature in the dark at 325 nm ($\varepsilon = 3930$ L mol^{-1} cm^{-1}). The wavelength is in good agreement with that in Bromley and Boxall studies.[46]

Infrared Spectroscopy. Infrared spectra (see Supporting Information) were measured on a PerkinElmer Spectrum Two spectrometer between 4000 and 400 cm^{-1}, equipped with a diamond attenuated total reflectance accessory.

NMR Spectroscopy. All NMR data were collected using a Bruker Avance 300 instrument with 300, 101, and 121 MHz for ^{1}H, ^{13}C, and ^{31}P, respectively. Multiplicities for coupled signals are denoted as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

Mass Spectrometry. Mass analysis was done using a ToF-SIMS V (ION-TOF GmbH, Germany) spectrometer with Bi^{3+} as the ionization source (25 keV, 0.4 pA).

X-ray Diffraction. X-ray diffraction analysis was performed on a D8 Advance Bruker diffractometer ($\theta-2\theta$ mode, Cu$_{K\alpha1/\alpha2}$ radiation) equipped with a Vantec1 linear position sensitive detector (PSD).

SEM−EDS Analysis. Scanning electron microscopy of ashes was performed using a Hitachi S-3400N (Hitachi High Technologies, Krefeld, Germany). A representative portion of each sample was deposited onto double-sided carbon tape mounted on a SEM support. Each sample was characterized by selecting two or three fields of view and examining the sample within them. The Ce/P ratio and morphology were noted and compiled for each sample. Scanning electron microscopy of airborne released particles was carried out using a JEOL JSM 6010-LV (with an acceleration tension of 20 kV). Sampling substrates (cellulose acetate membranes, SARTORIUS 11106-47-N, or transmission electron microscopy grids, Agar Scientific) were deposited onto double-sided carbon tape mounted on a SEM support. Each sample was analyzed over a large range of surfaces and SEM micrographs. EDX spectra were recorded for each particle denoting significant cerium content.

Synthesis of the Ce(IV)−NO$_3$−TPB$_{(org)}$ Complexes. To a solution of 2.00 g of ceric ammonium nitrate (3.65×10^{-3} mol) in acetonitrile (80 mL), 1.92 g of tributylphosphate (7.21×10^{-3} mol) is added. The solution is stirred and heated to 50 °C for 20 min and then evaporated to dryness. The orange oily residue is dissolved in chloroform (50 mL) to solubilize the orange oil, and the insoluble salt of ammonium nitrate that appears is removed by filtration and washed twice with chloroform (2 × 25 mL). The filtrate is evaporated to dryness and dried under vacuum to yield Ce$_2$O·6NO$_3$·3TBP$_{(org)}$ or Ce$_4$O$_4$·8NO$_3$·6TBP$_{(org)}$ as an orange oil (3.07 g, 92%).

The NMR spectroscopy analysis provide: ^{1}H NMR (300 MHz, CDCl$_3$, 300 K) δ (ppm) = 0.94 (t, 9H, C$\underline{H}_3$), 1.42 (m, 6H, C$\underline{H}_2$CH$_3$), 1.71 (m, 6H, OCH$_2$C$\underline{H}_2$), 4.24 (s(broad), 9H, OC$\underline{H}_2$).

Extraction Procedure. A solution of 10 mL of 7.14×10^{-2} mol L^{-1} ceric ammonium nitrate dissolved in 1 or 4 mol L^{-1} aqueous nitric acid is added to a mixture of 3 mL of TBP and 7 mL of HTP inside a closed thermostated cell heated to a fixed temperature. The biphasic solution is stirred for a certain amount of time either in the dark or in the presence of ambient light and the two phases are then separated for cerium content analysis.

Quantitative Analysis of Cerium in Aqueous Solution. The Ce^{4+} concentration in aqueous solution was determined using a potentiometric titration technique with sodium oxalate as a reducing agent and primary standard. The Ce^{3+} concentration in aqueous solution was determined by oxidizing all Ce^{3+} in Ce^{4+} with an excess of AgO (ca. 4.5 equiv), which can be reduced by heating. The solution was then titrated with a sodium oxalate solution of known concentration. Both methods have already been documented in the literature.[47,48]

Spectrophotometric Determination of Cerium Concentration in Solution Using Arsenazo-III. The total cerium concentration in both organic and aqueous solutions was determined using a spectrophotometric method using the Arsenazo-III dye.[29] Organic cerium(IV) can be quantified by back-extraction from the TBP/HTP solution by reduction to cerium(III). The organic phase is brought into contact with a

reducing 1% ascorbic acid aqueous solution, and the cerium content in the aqueous phase is analyzed. In a typical procedure, 1 mL of 10^{-4} M Arsenazo-III solution and 1 mL of 0.05 M glycine/HCl buffer solution are added in a 5 mL volumetric flask. A small volume (20–100 μL) of Ce^{3+} solution of unknown concentration is then added and the pH is checked to make sure it stands between 3 and 4. The volume is completed to 5 mL with deionized water and the absorbance of the solution is measured at 653 nm, using a reagent blank. Cerium concentration is then determined by exploiting Beer–Lambert's law along with an appropriate calibration curve. The calibration curve was plotted using a set of Ce(III)-$(NO_3)_3(H_2O)_6$ solutions of known concentrations complexed with the Arsenazo-III dye. The absorbance of these solutions is then measured by spectrophotometry, and the calibration curve is then established at the λ_{max} (653 nm) of the Ce(III)–Arsenazo complex.

Combustion Procedure. In a typical combustion experiment, a solution of 40 mL of 7.14×10^{-2} mol L^{-1} of ceric ammonium nitrate dissolved in a 4 mol L^{-1} nitric acid solution was shaken in a dark bottle with a mixture of 12 mL of TBP and 28 mL of HTP (3:7 volume ratio) for a few minutes. The biphasic medium was either used as is or separated to yield only an organic phase. Then, the liquid was poured into a cylindrical stainless steel container (h = 20 mm, ø = 90 mm) and allowed to rest for a few seconds, before igniting it with a propane blowtorch under an ambient atmosphere. The combustion was either stopped by smothering the fire with a metallic plate or allowed up to complete combustion. The remaining liquid residues were cooled before separation for further analysis and their respective volumes were measured in a graduated cylinder. Residual ashes deposited around the combustion container were also collected for analysis. Still images of identical experimental fires were taken at various time intervals using a Pyrex Petri dish.

Phosphoric Acid Molybdate Assay. To assess the presence of phosphate, a drop of the solution to be tested is added into a test tube containing 1 mL of 4 mol L^{-1} nitric acid. A spatula tip with ammonium heptamolybdate is introduced and the color of the solution is checked for the apparition of a characteristic yellow precipitate of phosphomolybdate.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00746.

> Calculations for the determination of the partition coefficient and of the kinetics experiments fitting; Figure S1 shows images of the color evolution of cerium in a biphasic HNO$_3$–TBP/HTP solution; Figure S2 presents the evolution of cerium(IV) concentration in 4 M HNO$_3$ at 70 °C; Figure S3 shows visible spectra of TBP/HTP, TBP/HTP saturated with HNO$_3$, and Ce(IV)–NO$_3$–TPB$_{(org)}$ in TBP/HTP saturated with HNO$_3$; Figure S4 shows the evolution of the absorbance of the Ce(IV) complex at various temperatures; Figure S5 indicates the behavior of the mixture during the combustion; Figure S6 illustrates the evolution of the temperature in a biphasic fire as a function of time; Figure S7 presents the ^{1}H NMR spectra of TBP, HTP, and TBP/HTP before and after combustion; Figure S8

displays the IR spectrum of a combustion soot sample; Figures S9 and S10 display the positive and negative mass spectra of a soot sample, respectively (PDF)

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Notes

The authors declare no competing financial interest.

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